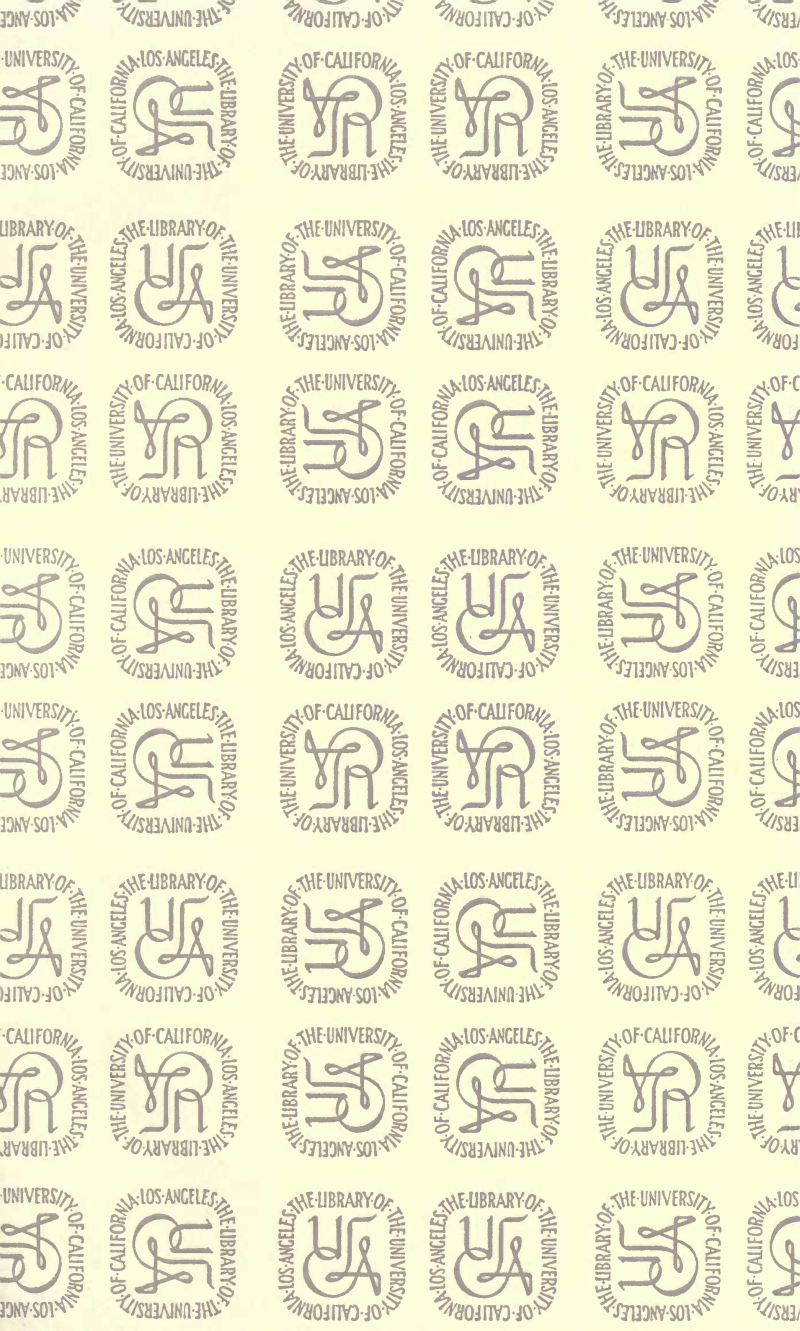


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Studies in the Adsorption of Charcoal

A DISSERTATION

PRESENTED TO THE FACULTY OF PRINCETON UNIVERSITY IN
CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

BY

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STUDIES IN THE ADSORPTION BY CHARCOAL.

I. THE RELATION OF SERVICE TIME TO ADSORPTION AND ABSORPTION.

Introduction.

Because of the prominence of gas warfare in the recent world war, means of protection against gas had to be developed. Naturally charcoal played a prominent part because of its remarkable properties as an absorbent. Also naturally one sample of charcoal prepared in one way might be better than another for a given use and the test developed to show superiority of one charcoal over another became known as the "service time" test. This method of testing has been described by Lamb, Wilson, and Chaney¹ and was purely an empirical test developed to approximate field conditions. Briefly, it consisted in passing air containing a known concentration of a toxic gas, as chloropicrin, at a definite rate through a sample of charcoal of standard dimensions until the gas could be detected in the effluent air. The test gave the desired data but had no theoretical basis, though many speculations had been made on this point. No known property of a charcoal could, however, lead one to say that it would give a better test than another without actually submitting it to these empirical conditions.

The lack of relation between service time and some physical properties of various charcoals is shown in Table I.

¹ *J. Ind. Eng. Chem.*, 11, 430 (1919).

TABLE I.¹

	A909.	Nela.	English.	German.
Density:				
True.....	1.84	1.89	1.86	1.70
Apparent.....	0.55	0.46	0.13	0.24
Vol. capillaries per cc.....	0.23	0.31	0.39	0.38
Service Time:				
Cal. minutes (accelerated).....	17.3	53.5	8.8	60.2 ^a
% wt. C(NO ₂)Cl ₃ at break point.....	14.6	48.7	32.0	110.0 ^a

^a This value was obtained not on the charcoal as taken from the canisters but after having been treated as described later.

Most of the speculations on service time have connected this property with either the well known great adsorptive power of charcoal or with capillary action due to its porous structure. We wished to investigate this relation and decided to measure the adsorptive power of these charcoals for nitrogen, carbon dioxide and water vapor. These were chosen because they were well defined, stable substances not very difficult of preparation in the pure state, and were widely different as to critical temperatures. Attention is called to this fact that at 25°, the temperature chosen for the measurements, water is normally a liquid, carbon dioxide is a gas just below its critical temperature, and nitrogen a gas and far above its critical temperature.

It was also realized that we had an opportunity to obtain adsorption measurements on charcoals which had been prepared in a very definite way and their other characteristics determined in the work on the various charcoals used for gas masks. Previous measurements, as given in the literature, may be considered to have doubtful value because of their non-reproducibility, since no special attention was given to the preparation of the charcoal, to activation, and to the other physical properties of the charcoal. Only in this sense was it intended to supplement the

¹ NOTE.—The method of determination of these properties follows:

True Density.—Charcoal placed in sample tube and evacuated at 445° and sealed *in vacuo*. Weighed in air, then opened under water and, after the "drift" had disappeared, the weight determined, and volume obtained from weight of water displaced (THIS JOURNAL, 42, 391 (1920)).

Apparent Density.—These figures are calculated on a moisture- and gas-free basis.

Volume of Capillaries.—Values obtained by centrifuging the sample of charcoal opened under water in the density determination for a definite period of time and approximately 1000 r. p. m. The excess weight of the sample over the true weight of the charcoal represented the water retained by the capillaries and is essentially the same as if the external water were removed by filter paper.

Service Time.—These tests were made by Dr. N. K. Chaney, of the National Carbon Co., by the standard accelerated method except that the rate was 500 cc. per minute instead of the usual 1000 cc., *i. e.*, the test is only half as accelerated as the standard. From the actual weight of the chloropicrin absorbed, the minutes service was calculated. We wish to express here our sincere thanks to Dr. Chaney for furnishing us with this data.

enormous amounts of data already collected on the adsorption of gases by charcoal. Special interest, however, was attached to the adsorption of water vapor, first because no accurate measurements of the adsorption of vapors by charcoal, which could normally exist as liquids at the temperature of the measurements, have previously been recorded in the literature, and secondly, because the so-called toxic "gases" of warfare were usually such vapors.

Description of the Charcoals.

A909.—This charcoal was prepared at Astoria in August, 1918, from cocoanut shells. The preliminary carbonization was at 950° for 10 hours. The sample was then steam-activated at 950° for 45 minutes according to a method described in detail elsewhere.¹ The sample used was 18–20 mesh, *i. e.*, that which would pass through an 18-mesh screen but was retained by a 20-mesh screen.

A909 Es.—This was the same charcoal as the preceding, the only difference being in the size of the particles. It was prepared by grinding the coarse A909 in a ball mill and collecting by electrical precipitation the dust which was too fine to settle.² The maximum diameter of the particles as determined microscopically was one micron, 0.001 mm.

Nela.—This was a mixture of cocoanut charcoals prepared and activated in the C. W. S. Laboratory at Nela Park, Cleveland. The charcoals composing this mixture were very similar but of various degrees of activity. The preliminary carbonization was made at 950° for 10 hours and the charcoals were then activated with steam at 950° for approximately 45 minutes.

English.—This was a mixture of English charcoals which were very similar. These charcoals were made from birch wood in gas retorts, that is, they were really air activated. The method of preparation was the standard adopted for the preparation of British war charcoals.

German.—For the details of the method of preparation of this charcoal, the reader is referred to an article by J. F. Norris.³ Briefly, the carbonization was affected as follows. The wood in pieces of uniform size was soaked in a hydrochloric acid solution of zinc chloride for about $1\frac{1}{2}$ hour. The acidified wood was then heated in a closed muffle furnace at a cherry-red for at least 6 to 8 hours. The charcoal obtained was washed with hydrochloric acid until the soluble ash was reduced to a minimum. The finished product contained about 0.01% of zinc. It was finally washed free from acid, drained on a grill, and dried in a vacuum at 70° to 80° . This sample of charcoal was taken from unused canisters which had been captured in September, 1918, and was further treated

¹ *J. Ind. Eng. Chem.*, **11**, 430 (1919).

² *J. Am. Chem. Soc.*, **42**, 391 (1920).

³ Norris, *J. Ind. Eng. Chem.*, **11**, 829 (1919).

before using it in the measurements, including those of the service time, as follows. It was boiled in distilled water for 2 hours, its water decanted and this treatment repeated 7 times. It was then boiled for 3 hours in dil. (1 : 7) hydrochloric acid, the acid decanted and then again treated as at first 3 times with water. It was dried in the air on filter paper, and then for 5 hours at 110–115° in air free from carbon dioxide and water vapor.

Preparation of Nitrogen, Carbon Dioxide, and Water.

Nitrogen.—A mixture of air with hydrogen from a Kipp generator using dil. hydrochloric acid and zinc metal, was forced through a combustion tube in the proper proportions to remove completely the oxygen and hydrogen, using copper-copper oxide as the indicator.¹ The effluent gases, nitrogen and argon, were collected and stored in a large glass gasometer over a dil. alkaline pyrogallate solution in order that they might not be contaminated with the oxygen originally dissolved in the water. Subsequent analysis showed no traces of oxygen, carbon monoxide, carbon dioxide, or hydrogen. Assuming that the air originally contained 78% of nitrogen and 1% of argon, the "nitrogen" used contained 1.25% argon. The gas, as used, was dried by passage over calcium chloride and phosphorus pentoxide.

Carbon Dioxide.—The carbon dioxide was prepared by dropping 1 : 1 sulfuric acid, kept in an atmosphere of carbon dioxide, on a saturated solution of sodium hydrogen carbonate. The sulfuric acid had been previously saturated with carbon dioxide to displace the dissolved gases. The gas was dried over calcium chloride and phosphorus pentoxide. Analysis showed a residue of less than 0.1% of gas not absorbed by a caustic potash solution. The gas was generated as used.

Water.—The water used was ordinary distilled water freed from dissolved gases as follows. About 10 cc. of distilled water was placed in the tube T, Fig. 1, and the system partially evacuated through the stopcock M by means of a Töpler pump. The water was then carefully frozen with solid carbon dioxide and ether and the system evacuated to the vapor pressure of water at that temperature. After closing the

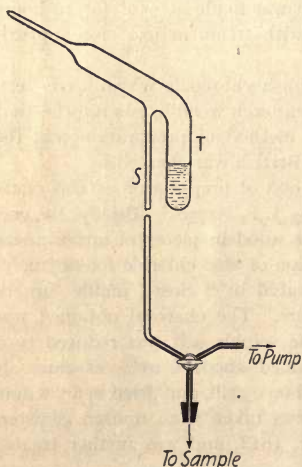


Fig. 1.

¹ *J. Am. Chem. Soc.*, 27, 1415 (1905).

stopcock M, the ice was allowed to melt and M opened again momentarily. Any air dissolved in the water would be given up to the vacuum. To remove this air, which was always less than 0.02 cc., the water was again frozen and the system re-evacuated.

Description of Apparatus.

A diagram of the apparatus is shown in Fig. 2. This consisted of a quartz tube, NP, 15 mm. inside diameter, and about 25 cm. in length. The sample of charcoal was placed in the lower 8 to 10 cm. of the tube and above this, in order to reduce the amount of dead space as much as possible, there was placed another quartz Tube, O, sealed at both ends and fitting tightly in NP. A ground glass, vacuum-tight joint at N joined the quartz tube containing the sample to a 3-way Stopcock, M. By means of this stopcock, the charcoal could be directly opened to the reservoir holding the gas to be absorbed or to a manometer S and through the stopcock R to a Töpler mercury pump, by which the evacuation of the system was effected. Pressures from a fraction of a millimeter to 400 mm. could be read from the manometer by means of a cathetometer and a scale placed between the 2 arms of the manometer. The pressure was read to the nearest 0.1 mm. The volume of the apparatus enclosed by the stopcock R and the quartz tube NP was measured directly by putting the quartz tube and filler, O, in place empty, with R closed and the system evacuated to R, and subsequent opening of R and evacuation of the rest of the apparatus, the gas being collected at the delivery of the pump and measured in a gas buret to the nearest 0.01 cc. Since the inside diameter of the manometer was previously measured and was of uniform bore, the volume of the apparatus at 0 mm. pressure could be calculated, as also the increase in volume with each millimeter pressure. For determining the free space in the apparatus when the charcoal was in place, the volume of the charcoal, calculated from the weight of the gas- and moisture-free sample and its previously determined true density, was subtracted from these values.

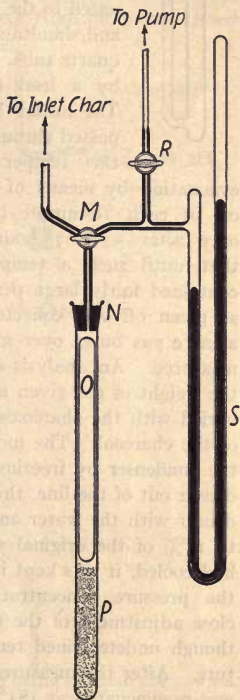


Fig. 2.

Method.

In practice, a sample of charcoal, containing an unknown weight of gas and moisture, was weighed directly into the quartz tube NP. The weight of the sample used depended on the apparent density of the charcoal since the volume of the charcoal used was a constant—about 14 cc. In the line between the pump and the stopcock R was sealed a small glass

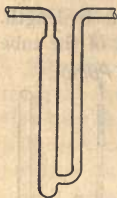


Fig. 2a.

condenser (Fig. 2a), which was immersed in solid carbon dioxide and ether after the system had been completely evacuated to the stopcock M. This stopcock was then opened and simultaneously an electric heater was placed around the quartz tube, the ground glass connection at N being cooled by a lead coil through which cold water was passing. The heater had been calibrated and sufficient current was passed through to raise the sample of charcoal to 750° and this temperature was maintained until, with continual evacuation by means of the Töpler pump, less than 0.1 cc. was given off in each 10-minute interval. This condition was usually obtained only after 5 to 7 hours heating. Previous experience had shown that until such a temperature had been reached the effluent gases contained fairly large percentages of the oxides of carbon. The gas as given off was collected at the delivery of the pump and stored in a large gas buret over mercury, in which the total volume of gas was measured. An analysis of a sample of this allowed easy calculation of the weight of gas given up by the charcoal during the treatment. This varied with the charcoals used from 1% to 10% of the original weight of the charcoal. The moisture in the charcoal, having been retained in the condenser by freezing, was determined directly by cutting the condenser out of the line, the stopcock R being closed, and weighing the condenser with the water and then empty. This moisture varied from 1% to 13% of the original weight of the charcoal. After the quartz tube had cooled, it was kept immersed in a thermostat at $25^{\circ} \pm 0.2^{\circ}$, while the pressure concentration measurements were being made. Fairly close adjustment of the temperature was necessary because of the large though undetermined temperature coefficient of pressure with temperature. After the measurements with one gas were obtained, the charcoal was re-evacuated at 184° (aniline b. p.) to remove the last traces of the adsorbed gas.

Admission of Nitrogen and Carbon Dioxide.

Since both these substances are gases, their pressures and concentrations were measured similarly, though necessarily differently from the method followed with water, a description of which will be given later.

For the admission of nitrogen, the apparatus shown in Fig. 3 was sealed to the stopcock M (Fig. 2). This apparatus consisted essentially of a

small gasometer, R, of known volume, kept immersed in a jacket of water NP, the temperature of which was recorded by the thermometer, T. The rest of the apparatus was the large gasometer in which the nitrogen was stored, and drying tubes containing calcium chloride and phosphorus pentoxide. By opening the stopcock, M, this apparatus, including the small gasometer R, could be completely evacuated to J. The line was then "washed out" several times with nitrogen from the large gasometer. When this was accomplished, the small gasometer was opened to the nitrogen supply and simultaneously the line to the gasometer from the pump closed

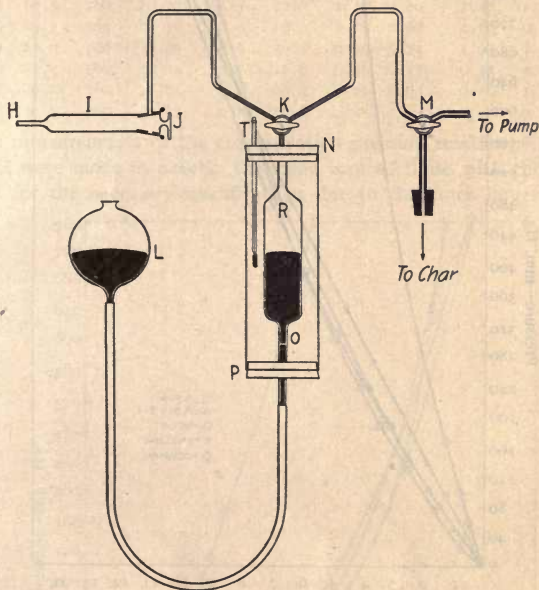


Fig. 3.

by turning the 3-way stopcock K. The stopcock J being opened, the gasometer R was filled with nitrogen to the zero mark at atmospheric pressure by means of the leveling bulb L. The temperature and pressure of this volume being known, it was readily reduced to N. T. P. The volume of the gasometer was 94.62 cc. Now the stopcocks K and M were so turned as to connect the sample of charcoal with the nitrogen in the gasometer and the levels of mercury in L and R kept approximately level while the gas was being adsorbed. Equilibrium was very rapidly reached and the 2 levels carefully adjusted. The stopcock M was then turned so the line

between K and M and the gasometer R could be evacuated. In this way the excess of gas remaining in the gasometer could be measured by collecting it as pumped off at the delivery of the Töpler pump and its volume determined in a gas buret. By subtracting this volume, corrected to N. T. P., the amount of nitrogen in the quartz tube NP, Fig. 2, was known, and by subtracting from this value the nitrogen in the previously determined free space of the tube, also corrected to N. T. P., the amount of nitrogen in cc. N. T. P. adsorbed at 25° and atmospheric pressure was

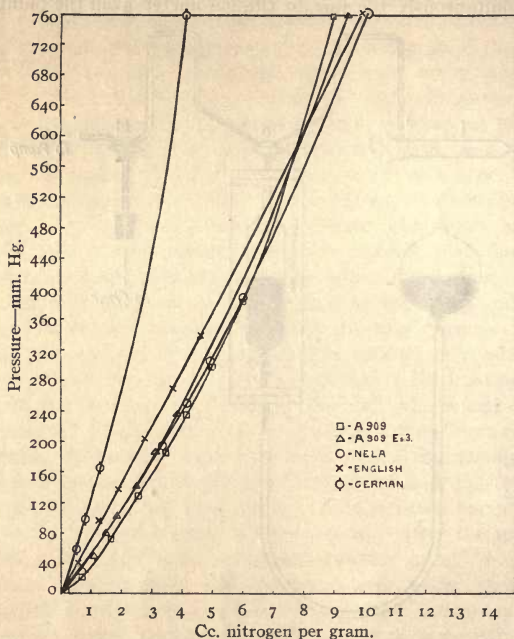


Fig. 4.—Adsorption isotherms for nitrogen on charcoals at 25° .

determined. By a series of evacuations, and collecting and measuring each volume of gas as pumped off, and subtracting this from the previous volume of gas in the system, the amount of nitrogen in the system at several pressures could be measured. Since the volume of the system was known for each pressure, the volume of nitrogen adsorbed on the charcoal could be easily calculated. The nitrogen could be completely pumped off at 25° . A typical table is given in Table 2 as an example of the method of recording results. Fig. 4 represents the concentration

pressure curves for nitrogen as plotted from the data obtained with the various charcoals.

TABLE II.
Adsorption of Nitrogen by A909 Es. 3.

	Cc. admitted.		Cc. N. T. P.	Press. Mm. Hg.	Room temp.	Vol. system.		Gas in Sys. N. T. P.	Gas on char.	Cc. gas per g.
	T.	P.				Bulb.	Line.			
75.89	19.0	760	70.99	760.0	10.66	10.66	60.33	9.46
32.38	19.5	760	30.21	235.8	19.8	3.32	2.58	5.90	24.31	3.84
26.06	19.5	760	24.32	186.0	19.8	2.67	1.83	4.50	19.82	3.11
20.38	19.5	760	19.01	142.0	20.0	1.99	1.26	3.25	15.76	2.48
14.97	19.5	760	13.97	101.5	20.0	1.42	0.80	2.22	11.75	1.84
11.96	19.7	760	11.16	80.0	19.7	1.12	0.60	1.72	9.44	1.48
8.62	20.0	760	8.03	48.9	20.3	0.69	0.34	1.03	7.00	1.10
4.66	20.2	760	4.34	21.7	20.6	0.30	0.13	0.43	3.91	0.61
1.98	20.2	760	1.84	5.1	20.3	0.07	0.03	0.10	1.74	0.27
0.18	20.3	760	0.17	0.2	20.6	0.17	0.03

The measurements of the concentration pressure relation with carbon dioxide were made in exactly the same way as those with the nitrogen except for the necessary modifications due to the much larger amounts

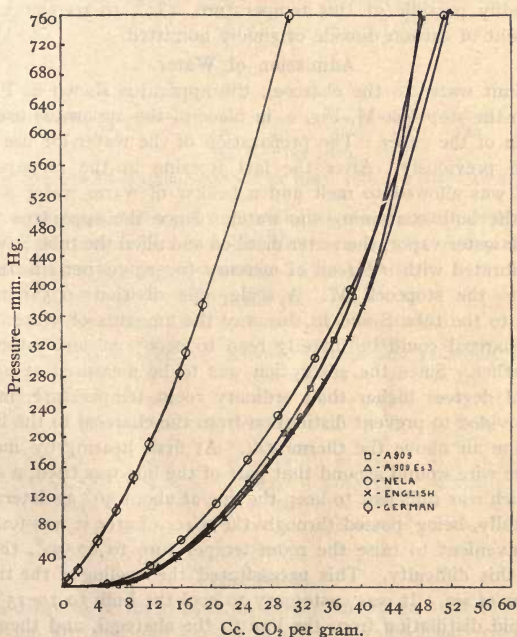


Fig. 5.—Adsorption isotherms for carbon dioxide on charcoals at 25°.

adsorbed. This necessitated several fillings of the gasometer R. For the admission of carbon dioxide, the generator was sealed to the apparatus shown in Fig. 3 at H. The generator was furnished with a mercury valve immediately before a stopcock which separated it from the rest of the system. Carbon dioxide was generated and allowed to escape through this valve until tests showed that the gas was completely adsorbed by a caustic potash solution. The concentration pressure curves obtained for carbon dioxide on the different charcoals are shown in Fig. 5. It was found that the complete removal of the carbon dioxide from the charcoal at the temperature of adsorption was a slow and tedious process. The gas came off very slowly at the lowest pressures, as much as 8 cc. per g. of charcoal being retained by one of the charcoals at a pressure of 1.4 mm. Hg. The only exception to this was in the case of the German charcoal, with which the amount adsorbed per g. was about half that of the amount adsorbed by the other charcoals, and where the carbon dioxide was readily pumped off at 25°. In order, therefore, to free the surface from adsorbed gas, the tube was immersed in a tube of boiling aniline vapor. It was very readily possible at this temperature, 184°, to recover completely the amount of carbon dioxide originally admitted.

Admission of Water.

To admit water to the charcoal, the apparatus shown in Fig. 1 was sealed to the stopcock M, Fig. 2, in place of the apparatus used for the admission of the gases. The preparation of the water for use has been described previously. After the last freezing in the preparation, the ice in T was allowed to melt and a beaker of warm water was placed around the bulb containing the water. Since the apparatus was filled only with water vapor, the water distilled and filled the tube S, which had been calibrated with a thread of mercury (0.123 cc. per cm. tube) completely to the stopcock M. A scale—one division=0.581 mm., was fastened to the tube S and in this way the amounts of water admitted to the charcoal could be directly read to 0.007 cc. and estimated one place farther. Since the adsorption was to be measured at 25°, which is several degrees higher than ordinary room temperature, means had to be provided to prevent distillation from the charcoal to the line which was in the air above the thermostat. At first, heating by means of a Nichrome wire wound around that part of the line was tried, a small current, which was sufficient to keep the line at about 30° as determined experimentally, being passed through the wire. Later it was found to be more convenient to raise the room temperature to 27–30°, thereby removing this difficulty. This necessitated the cooling of the thermostat by means of ice. It was customary to cool the bulb to 10–15°, causing more rapid distillation from the line to the charcoal, and then allowing the temperature to slowly rise. The pressure was read when the tem-

perature reached 25° . As this pressure approached that of water at 25° , 23.5 mm., it was sometimes necessary to repeat this cooling before the pressure would remain constant. It frequently required 3 to 5

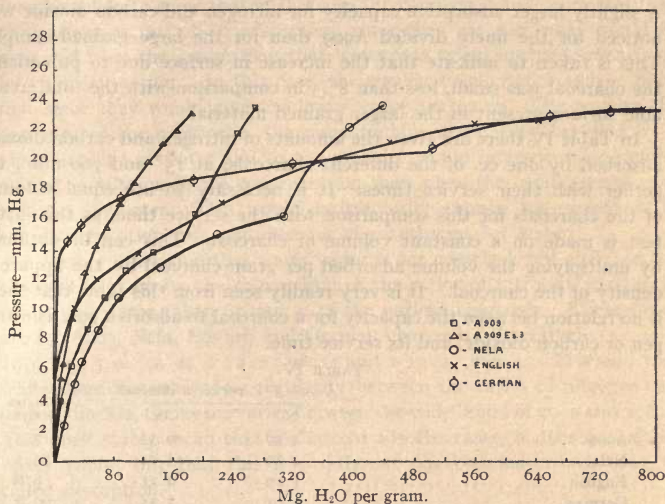


Fig. 6.—Adsorption isotherms for water vapor on charcoals at 25° .

hours for equilibrium to be reached. The curves of concentration pressure of water on the various charcoals are shown in Fig. 6. A typical table of experimental data is also appended in Table III:

TABLE III.
Adsorption of Water by English Charcoal at 25° .

Cc. of water admitted.	Pressure mm. Hg.	Room temp.	Cc. of water in system.	Cc. of water on charcoal.	G. of water on charcoal.	G. of water per g. of charcoal.
0.0357	10.2	27.8	0.00015	0.0355	0.0354	0.0277
0.0743	12.1	29.2	0.00015	0.0741	0.0738	0.0577
0.1458	13.8	29.6	0.00017	0.1456	0.1449	0.1133
0.2886	17.2	30.4	0.00026	0.2883	0.2872	0.2247
0.4314	19.8	29.4	0.00030	0.4311	0.4295	0.3360
0.5742	21.2	29.6	0.00032	0.5739	0.5720	0.4473
0.7184	22.4	30.2	0.00034	0.7181	0.7156	0.5595
0.8262	22.6	30.3	0.00034	0.8259	0.8230	0.6441
1.0047	23.4	29.9	0.00036	1.0043	1.0009	0.7831

Discussion.

A consideration of these data on adsorption shows that the isotherms obtained for nitrogen and carbon dioxide on the various charcoals are of the same general form as previously obtained by other investigators,

i. e., Homfray,¹ Titoff,² Travers,³ Baerwald.⁴ Furthermore, the quantities adsorbed do not vary much among themselves for equal weights of the various charcoals, except for the specially treated German charcoal. A slightly larger adsorptive capacity for nitrogen and carbon dioxide was noticed for the finely divided Ag99 than for the large grained sample. This is taken to indicate that the increase in surface due to pulverizing the charcoal was small, less than 8%, in comparison with the total available surface present in the larger grained material.

In Table IV there are given the amounts of nitrogen and carbon dioxide adsorbed by one cc. of the different charcoals, at 25° and 760 mm., together with their service times. It is necessary to use equal volumes of the charcoals for this comparison with the service time, as this latter test is made on a constant volume of charcoal. This can be obtained by multiplying the volume adsorbed per gram charcoal by the apparent density of the charcoal. It is very readily seen from this table that there is no relation between the capacity for a charcoal to adsorb a gas, as nitrogen or carbon dioxide, and its service time.

TABLE IV.

	Cc. N. T. P. per cc. of charcoal.		Minutes service.
	N ₂ .	CO ₂ .	
Ag99.....	4.97	26.53	17.3
Nela.....	4.89	25.04	53.5
English.....	1.29	6.21	8.8
German.....	1.01	7.35	60.2

In the exponential formula, $q = a.p^{1/n}$, for adsorption isotherms, Titoff⁵ found that the value of n is very close to unity for gases which at ordinary temperatures may be called "perfect gases" and that it increases in value for gases of increasingly high critical temperatures. This would give approximately a straight line to the isotherms of the perfect gases and the curves would become more and more concave to the pressure axis for gases with increasingly higher critical temperatures. If this generality could be applied even to cases where the measurements were made on a vapor which could exist normally as a liquid under the conditions of the measurements, as water in our experiments, we should expect that the isotherm for water would be very much more concave to the pressure axis than that for carbon dioxide. However, the curves obtained for water are of a form exactly opposite, that is, they are concave to the concentration axis.

Charcoal, being of a porous nature, besides presenting enormous sur-

¹ Homfray, *Z. physik. Chem.*, 74, 129 (1910).

² Titoff, *ibid.*, 74, 641 (1910).

³ Travers, *Proc. Roy. Soc.*, 78, 9 (1907).

⁴ Baerwald, *Ann. Physik*, 23, 90 (1907).

⁵ *Loc. cit.*

face and accordingly having high adsorptive capacity, also offers the opportunity of capillary action, especially to the vapor of a liquid which has as high a surface tension as water. The isotherms for water must, therefore, be taken to show that in this case the capillary action is greater than the surface attraction of adsorption, since they are just what would be expected from the assumption that water was taken up predominately by capillary action. In this case, the smaller capillaries would be filled first since they would give the lower vapor pressures. The smaller the diameter of the capillaries, the more rapidly would they be filled by a given amount of water and so the pressure would increase more rapidly at first in relation to the concentration than when the capillaries were of a larger diameter. This would satisfactorily explain the concavity to the concentration axis obtained for the isotherms for water.

A further indication that water vapor is not *adsorbed*, but *absorbed*, by charcoal is given by the comparison of the ratios of nitrogen, carbon dioxide, and water taken up per g. of the various charcoals. These ratios are for Ag99, Nela, English and German charcoals, respectively, 1 : 5.3 : 29.9; 1 : 5.0 : 54.2; 1 : 4.8 : 98.1; and 1 : 7.4 : 226.4. It is seen that while there is more or less regularity between the ratios of nitrogen and carbon dioxide, the water varies between the wide limits of 29.9 and 226.4. This must surely mean that if charcoal adsorbs gases, it does not *adsorb* water vapor, but that this is a different phenomenon, which may be called *absorption*.

A quite pronounced break can be seen in the isotherms for water on the different charcoals, with the exception of the finely divided Ag99. In a study on the "adsorption" of water by silica gel, Anderson¹ obtained a similar break. He seems justified, from his later work on the study of the velocity of adsorption, to conclude that this break marks the intersection of 2 phenomena, the first smooth part of the curve represents the taking up of water vapor by capillary action, the break occurs only when the capillaries have filled up and the further increase in vapor pressure is due merely to the flattening of the meniscus at the ends of the capillaries.

Anderson developed in his paper a formula which can be used for the calculation of the diameters of the capillaries from the vapor pressure measurements. By means of this formula, it is also possible to calculate the surface of the charcoal since the volume of each size capillary can be obtained directly by reference to the concentration axis. The formula is

$$r = \frac{2T \cdot s_0 \cdot 0.4343}{d \cdot p_0 \cdot \log(p_0/p_1)}$$

where r = radius of the capillary; T = surface tension in dynes per cm.

¹ Anderson, *Z. physik. Chem.*, 88, 191 (1914).

at $25^\circ = 72.1$; s_0 = vapor density of water vapor above water at $25^\circ = 22.75 \times 10^{-6}$; d = density of water at $25^\circ = 0.99707$; p_0 = vapor pressure in dynes of water at $25^\circ = 23.517 \times 13.534 \times 980.1 = 31.20 \times 10^4$; and p_1 = the vapor pressure in the capillary.

The lowest pressure measured in our experiments was 2.3 mm. on the Nela charcoal when 16 mg. of water had been absorbed per g. of charcoal. This corresponds to a capillary diameter of 9.1×10^{-8} cm. A vapor pressure of one mm. represents a pore with a diameter of 6.7×10^{-8} cm. In Table V are listed the smallest, largest and mean diameters of the capillaries in each charcoal, as calculated from this equation, together with the surface as calculated by applying this formula as indicated above.

TABLE V.
Capillary diameters.

	Capillary diameters.			Cal. surface.	
	Smallest. Cm.	Largest. Cm.	Mean. Cm.	Per g. M. ⁻²	Per cc. M. ⁻²
Agog.....	6.7×10^{-8}	4.1×10^{-7}	2.8×10^{-7}	230	130
Nela.....	6.7×10	5.5×10	3.7×10	440	200
English.....	1.6×10	1.9×10	8.3×10	300	40
German.....	2.0×10	1.3×10	9.5×10	160	40

Lamb, Wilson, and Chaney¹ have estimated that the surface of one g. of an activated charcoal is about 1000 square meters, which from our data would appear to be too great. Recently A. M. Williams,² in developing a new interpolation formula for the adsorption of gases, was able to calculate that the surface of the charcoal used by Dr. Ida F. Homfray³ was 131 square meters, which agrees well with the values we have obtained, especially when one considers that this was a pre-war product and not activated. With a surface of the magnitude given by our calculations, adsorption of nitrogen and carbon dioxide at ordinary temperatures and to pressures as high as atmospheric could well be in a monomolecular layer, such as is characterized as true adsorption by Langmuir,⁴ since 50 cc. of carbon dioxide at N. T. P. would occupy in a monomolecular layer a surface of less than 150 square meters. Also the fact that, while the differences in the calculated surfaces of Agog, Nela, and English charcoals is considerable, there is not a corresponding difference in the adsorption of the gases, this would make the concept of "elementary spaces" postulated by Langmuir⁸ necessary. The difference in the adsorptive capacity of a given charcoal for nitrogen and carbon dioxide would then depend solely on the difference in "time-lag" of the condensation evaporation process of adsorption.

Since it has been shown that the taking up of water vapor is a different

¹ Lamb, Wilson and Chaney, *J. Ind. Eng. Chem.*, **11**, 430 (1919).

² Williams, *Proc. Roy. Soc.*, **96A**, 287 (1919).

³ *Loc. cit.*

⁴ Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918).

phenomenon from adsorption, it is interesting to see whether there is any relation between this phenomenon, absorption, and service time. The necessary data for this comparison is collected in Table VI. In this table the per cent. weight of chloropicrin held by the charcoal at the break point, the saturation point, and the "retentivity" point are calculated to volume of chloropicrin. The retentivity signifies the amount of chloropicrin left in the charcoal on reversing the test until no trace of chloropicrin can be detected in the effluent air. The density of chloropicrin at 25° has been taken to be 1.651, the density determined at the American University being $d_4^{20} = 1.6539$.

TABLE VI.
Vol. chloropicrin in cc. at.

	Vol. chloropicrin in cc. at.			Vol. capillaries per g.	
	Break.	Saturation.	Retentivity.	Total.	At break in curve.
Ag99.....	0.0884	0.1762	0.0806	0.2728	0.1735
Nela.....	0.2948	0.4406	0.3083
English.....	0.1938	0.3967	0.0696	0.7828	0.6435
German.....	0.6561	0.8174	0.1726	0.8543	0.4948

Here, also, we see no relation between service time and capillary action. Further, there does not appear to be any relation between the volume of the capillaries and retentivity or saturation, except as might be expected the saturation occurs in each case before the capillaries were completely filled, due to the fact that the lower layers of charcoal had not yet reached saturation.

This complete lack of quantitative relation between service time with the phenomena of adsorption and absorption is not startling. The test, as developed, was only empirical and such factors as size of mesh of the sample and resistance to the passage of air were known to have a marked influence on the service time. It is this "sieve effect" of removing the vapors from the air that is the uncertain and indeterminate factor in the minutes service that a charcoal can give. We know of no other phenomena, however, which can explain the mechanism of this removal of gases, or vapors, of high critical temperature from those of much lower, than adsorption and absorption. We must conclude, therefore, that both of these phenomena are probably involved in the determination of service time, and, from our work on the absorption of water vapor, that capillary action predominates over the influence of unmodified surface action or adsorption.

Conclusions.

1. No relation between service time and adsorption of a gas, as nitrogen or carbon dioxide, by various charcoals has been found to exist.

2. Measurements of the adsorption of these gases by charcoals have shown that, according to the original preparation of the charcoal, the adsorptive capacity per gram of charcoal at 25° and 760 mm. may vary as much as 100%.

3. It has been shown that the adsorption of nitrogen and carbon dioxide by charcoal may be considered to be in a condensed layer one molecule deep.

4. Measurements of the isothermal adsorption of water vapor by charcoal at 25° show that water is not adsorbed by charcoal but is held by capillary action, *i. e.*, is absorbed.

5. Using Anderson's formula connecting the radius of a capillary with vapor pressure, the mean diameters of the capillaries of the 4 charcoals used have been calculated and have been found to vary between 2.8×10^{-7} cm. and 9.2×10^{-7} cm. The maximum diameter in any of the charcoals was determined to be 1.3×10^{-6} cm.

6. By means of this same formula and the isothermals for water, the surfaces of the various charcoals were found to vary from 160 square meters to 436 square meters per gram of charcoal.

7. It was pointed out that this variation in surface was not always accompanied by a corresponding variation in adsorptive capacity. This makes the concept of "elementary spaces" as postulated by Langmuir necessary.

8. No relation between the service time of the different charcoals with the volume of the capillaries was found. The same was true for the saturation point and the retentivity of these charcoals. This lack of relation must indicate that other indeterminate factors must influence largely the minute service of a charcoal; *i. e.*, the 2 phenomena, adsorption and capillary action are insufficient in themselves to explain this test.

STUDIES IN THE ADSORPTION BY CHARCOAL.

II. RELATION OF OXYGEN TO CHARCOAL.

De Saussure,¹ in one of the first quantitative measurements of adsorption by charcoal, was unable to obtain results for oxygen because it alone of the gases would not apparently come to equilibrium even after a year. This anomalous behavior in the adsorption of oxygen by charcoal has been largely overlooked by recent investigators though previously recognized and recorded by R. Angus Smith,² who found that the adsorption of oxygen continued for at least a month, though this was not true for hydrogen, nitrogen or carbon dioxide; and that, when it was sought to remove the oxygen by heat, carbon dioxide was given off in place of

¹ De Saussure, *Gilb. Ann.*, 47, 113 (1814).

² R. A. Smith, *Proc. Roy. Soc.*, 12, 424 (1863).

oxygen, by H. Kayser,¹ who found that the adsorption of oxygen had not reached an end after two weeks; and by J. Böhm,² who found that nitrogen absorbed by charcoal could be completely removed but that oxygen could be only partly removed "even by boiling water."

However, in the exhaustive work on adsorption by Dr. Ida F. Homfray,³ as in that of Baerwald⁴ and in that of Lemon,⁵ no such peculiarities in the behavior of oxygen were noticed. Dr. Homfray obtained equilibrium with the various gases in from a few minutes to $1/2$ hour, depending on the temperature, and so apparently missed this peculiar effect first recorded by De Saussure. These later investigators also were not concerned with the recovery of the adsorbed gases as such, so they did not observe the second peculiarity mentioned by Smith, *i. e.*, the fact that the oxygen may be recovered only partly as oxygen, the rest being recovered only as oxides of carbon.

In our work on the adsorptive power of the war charcoals we noticed this singular difficulty of obtaining equilibrium with oxygen. Furthermore, in attempting to determine the moisture and gas content of these charcoals,⁶ it was noticed that gases continued to be given off to a vacuum as the temperature was raised. Up to 900° , these gases consisted almost entirely of carbon dioxide and carbon monoxide, the first predominating at the lower temperatures and the latter at the higher. At about 1000° , carbon dioxide and monoxide practically ceased to be obtained. Above 1000° hydrogen began to be more noticeable and to come off in increasingly large quantities as the temperature was raised. The hydrogen was presumably from hydrocarbons undecomposed in the original preparation of the charcoals.

When a charcoal has been thoroughly "outgassed" at 900° to 1000° and allowed to cool to room temperature in a vacuum and gases admitted, it was found possible to recover completely such gases as hydrogen, nitrogen, and carbon monoxide at room temperature, though the rate at which they could be collected in a Töpler pump was increased by raising the temperature; 90% of the carbon dioxide could be recovered, and smaller percentage of the water, at room temperature, but both could be quantitatively obtained at 184° (aniline b. p.) as rapidly as possible to collect them with a Töpler pump for the carbon dioxide and with a condenser cooled with solid carbon dioxide for the water.

However, when oxygen was admitted and allowed approximately to come to equilibrium, only about half was recovered by evacuating at

¹ H. Kayser, *Wied. Ann.*, **12**, 526 (1881).

² J. Böhm, *Bot. Z.*, **1883**, 32-34.

³ F. Homfray, *Z. physik. Chem.*, **74**, 129 (1910).

⁴ Baerwald, *Ann. Physik*, **23**, 90 (1907).

⁵ Lemon, *Phy. Rev.*, [2] **14**, 281, 394 (1919).

⁶ C. W. S. Reports, Sept.-Dec., 1918.

room temperature and only traces on increasing the temperature to 184° , though on again cooling to room temperature and again admitting oxygen, this second lot was readily recovered. Therefore attempts were made to recover completely this oxygen, which had apparently disappeared, by increasing the temperature still further, and soon carbon dioxide and monoxide began to appear, but not until a temperature of 900° to 1000° was again reached was all the oxygen recovered and then *not as oxygen* but as these *oxides of carbon*. We have interpreted this to indicate that there were here 2 phenomena, adsorption and "fixation" or "combination" of the oxygen with the charcoal. The adsorbed oxygen was regarded as that which was recoverable by evacuating at room temperature, and the "fixed" oxygen that which was recovered only as the oxides of carbon at higher temperatures.

These facts led us to a more thorough investigation of this fixation of oxygen by charcoal, both as to the length of time necessary to reach saturation and also as to the amounts of oxygen which could be held in this way by the charcoal. For this purpose we used 3 samples of war charcoal described in the preceding paper as A909, English, and German. Their moisture and adsorbed gas contents were known, and the samples were kept in carefully stoppered bottles.

Experimental.

A. Determination of Equilibrium of Charcoal and Oxygen at 250 and 760 mm.—For this purpose, 3 bulbs of about 25 cc. capacity each were filled with the above named charcoals and each was sealed to a line which led either to a Töpler pump or to a buret containing pure electrolytic oxygen. Each bulb was separated individually from the line by a one-way stopcock, and during the measurements was kept immersed in a thermostat at $25^{\circ} \pm 0.1^{\circ}$. As a preliminary treatment, the samples were thoroughly freed from adsorbed gases by outgassing at 184° , leaving in them, however, the fixed oxygen they originally contained. When the bulbs had been cooled in the thermostat, oxygen was admitted at 760 mm. by a constant pressure arrangement. From the temperature of the buret, the amount of oxygen admitted to the bulb was reduced directly to N. T. P. After the first correction for the dead space in the bulb, the amount taken up each time was divided by the weight of the moisture and gas-free sample, reducing the results to cc. of oxygen per g. of sample.

Fresh oxygen was admitted from time to time and the amounts recorded. At the end of the first 100 hours, when the amounts of oxygen taken up at successive intervals were becoming less, each sample was evacuated thoroughly at 25° . In no case was the amount of oxygen originally admitted recovered. In some cases traces of carbon dioxide and carbon monoxide were found in the gases collected. Since the sam-

ples were largely oxygen, it was thought possible that the small amounts of carbon monoxide were from the alkaline pyrogallate used to absorb the oxygen. Oxygen was then admitted and its course followed. This was repeated until equilibrium was reached. This was most quickly reached by the English charcoal at the end of 1600 hours or 66 days, while the German charcoal took just about twice this length of time. The data is presented in the form of curves as shown in Figs. 1, 2 and 3.

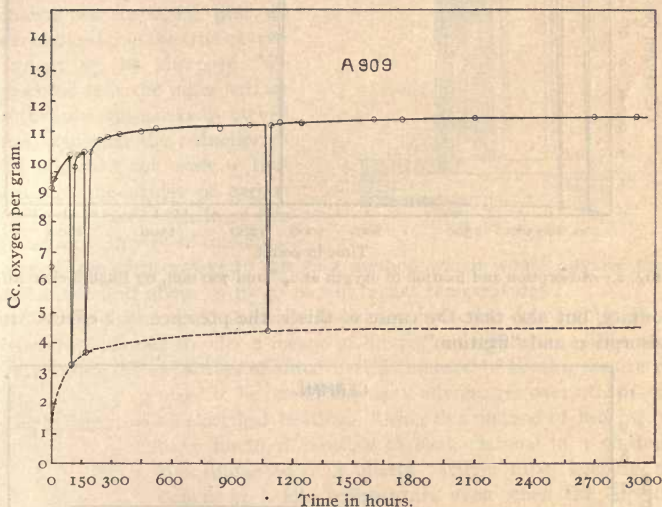


Fig. 1.—Adsorption and fixation of oxygen at 25° and 760 mm. by A909 charcoal.

It will be noticed that we really have 2 curves from each series of measurements. The upper curve represents in each case the total amount of oxygen taken up at 25° and 760 mm., while the lower dotted curve represents that which cannot be obtained by evacuation at 25°. It is also apparent that the slopes of the 2 curves are very similar. From our previous experience, we are led to the conclusion that the lower curve represents the rate of saturation of the charcoal by what we have called "fixed" oxygen, and that the upper curve is the sum of 2 effects, true adsorption and fixation. Since this is the case, it can readily be seen that the long time necessary to reach equilibrium is due to this fixation and that the true adsorption of oxygen by charcoal occurs as rapidly as for other gases.

These measurements have, therefore, shown not only that the equilibrium between oxygen and charcoal is attained only after months of

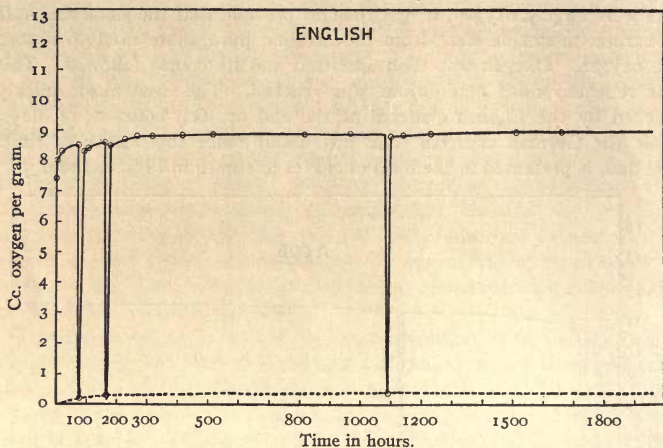


Fig. 2.—Adsorption and fixation of oxygen at 25° and 700 mm. by English charcoal.

contact, but also that the cause of this is the presence of 2 effects, true adsorption and “fixation.”

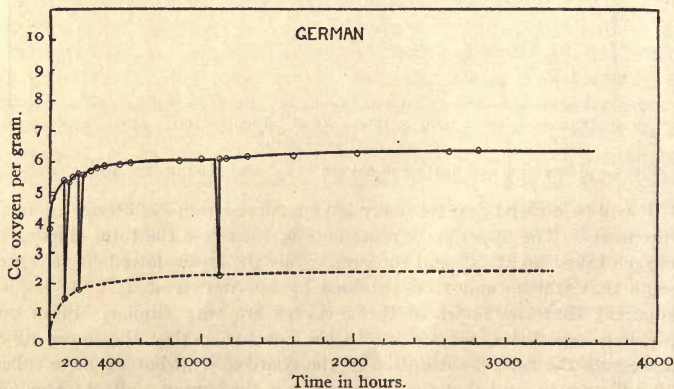


Fig. 3.—Adsorption and fixation of oxygen at 25° and 760 mm. by German charcoal.

B. Determination of Total “Fixed” Oxygen.—In order to obtain all the fixed oxygen from charcoal, it seemed necessary only to heat the sample in a vacuum, after first removing all the adsorbed gases and vapors, and to collect and analyze the evolved gases. The carbon dioxide and monoxide are calculated to cc. of oxygen, N. T. P., per g. of charcoal. The

procedure first adopted was as follows: the charcoal was heated in a fused quartz tube in an aniline bath and thoroughly outgassed, then in a Ni-chrome resistance furnace to 1050° . Gases continued to be slowly given off for several hours at this temperature and still contained small percentages of the oxides of carbon.

Since even at this temperature the charcoal acted on the fused quartz, we suspected that we were not getting the true oxygen content of the charcoal. We observed that the inner surface of the tube was markedly etched and suspected the reduction of the silica to a sub-oxide so that some of the oxides of carbon might well have been from this reduction. In view of this situation, it seemed necessary to devise a method which would obviate these difficulties and allow us to go to still higher temperatures.

The development of the high frequency induction furnace by E. F. Northrup¹ seemed to offer a means of solving our difficulties. The compactness of the apparatus afforded by this method of heating was recognized to be one of its many advantages over other forms of electrical heating. Using this method of heating, we have found it possible to heat charcoal in a platinum cup supported in a quartz vacuum tube, keeping the quartz at a low temperature even when the cup and charcoal were at 1400° . In this way the possibility of a leak through hot quartz and reduction of the silica to a sub-oxide were prevented.

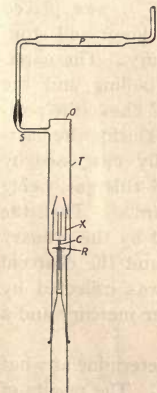


Fig. 5.

The apparatus designed for this experimental work is shown in Fig. 5. It consists primarily of a fused quartz tube, T, 25 cm. long and 2.5 cm. outside diameter, with a side tube, S, connected to a glass tube by a de Khotinsky joint leading to a Töpler pump through a phosphorus pentoxide tube, P. The upper end of the quartz tube was closed by an optically clear piece of fused quartz; and the lower end by a stopper of Pyrex glass with a ground joint, which also served indirectly as a support for a platinum-rhodium crucible, X. The crucible was 3.5 cm. long and 1.5 cm. in diameter and had a platinum pin riveted to the bottom. This pin fitted in a fine porcelain tube, C, which in turn was held in the Pyrex

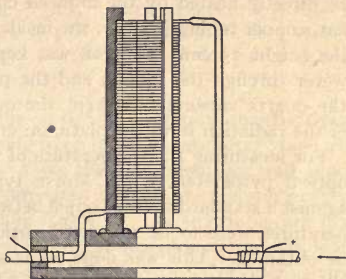


Fig. 4.

¹ Northrup, *Trans. Am. Electrochem. Soc.*, 35, 69 (1919).

support. In order to prevent radiation downwards, a porcelain disk, R, was fastened to the small porcelain tube. The crucible served as the resistor and was rapidly heated by the induced currents from the primary. When the charcoal was heated it also became a conductor and so could be directly heated by the induced currents. The primary was a coil of flat, copper tubing (Fig. 4), the inside diameter of which was 3.6 cm. and the height 15 cm. The coil was kept cool by passing a stream of cold water through the tubing, and the proximity of this coil to the walls of the quartz vacuum tube kept the quartz at a low temperature in spite of the radiation from the platinum crucible.

For measuring the temperature of the charcoal, a Leeds and Northrup optical pyrometer of the Morse type was used. This was calibrated against a standard thermocouple between 800° and 1400° . Since the temperatures were to be measured optically, black body conditions had to be obtained. This was done, as is shown in the cut, by placing a very thin, platinum truncated cone over the top of the crucible to minimize the radiation from the surface; and then a platinum tube of very thin foil of 0.4 cm. diameter was placed in the center of the sample and focusing was made on the surface of the charcoal at the bottom of this tube.

The procedure in making a determination was as follows: The crucible was filled with a known weight of charcoal and the apparatus assembled

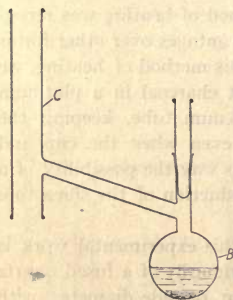


Fig. 6.

as described. The heater shown in Fig. 6, containing naphthalene (b. p. 218°), was placed around the quartz tube and the lower end stoppered and covered with mercury. The naphthalene was then brought to boiling and the vapors allowed to condense to C above the position of the platinum crucible. During the heating the charcoal was continually outgassed by means of the Töpler pump and this gas, being regarded as adsorbed gas, discarded. Then the naphthalene bath was replaced by the primary coil of the induction furnace and the charcoal heated rapidly. All the gas was collected by

the Töpler pump and was stored in a large gas buret over mercury and a sample of this analyzed.

A preliminary run was made on the Ag₂O in order to determine at what temperature the oxides of carbon ceased to be obtained. The results of this experiment are shown in Table I.

They show that the amounts of oxygen remaining combined with the charcoal above 1180° are extremely small and could be neglected. It seemed important to see what gases could be obtained at still higher temperatures, however, and so in 2 of the experiments the temperature was

raised to 1400°. The gas at these high temperatures was more than 99% hydrogen and was slowly decreasing in amounts obtained as the temperature was raised.

TABLE I.

	Total gas. Cc. per g.	Temp. limits.	Time of heating.	Cc. per g.				Fixed oxygen. Cc. per g.
				CO ₂ .	CO.	H ₂ .	CH ₄ .	
I....	36.42	200-1000°	2 hrs.	4.66	23.40	8.32	0.04	16.36
II....	17.60	1000-1180°	2½ hrs.	0.08	0.53	16.93	0.06	0.35
III....	4.87	1180-1260°	1¼ hrs.	0.00	0.07	4.76	0.04	0.03

Since the object of this part of the work was to obtain quantitatively the amount of oxygen capable of being fixed by charcoals, after standardization of the method with ordinary Ag99, the determinations were made on the 3 samples which had been saturated in pure electrolytic oxygen. The results obtained are presented in Table II. In this table are first given the results from 2 successive runs on two samples of Ag99 in order to get some idea as to the reproducibility of the results. Considering that charcoal is not a pure substance, the agreement is regarded as very good

TABLE II.

	Total gas. Cc. per g. (N. T. P.)	Maximum temp.	Time of heating.	Cc. N. T. P. per g.				Fixed O ₂ per g		
				CO ₂ .	CO.	H ₂ .	CH ₄ .	Cc.	N. T. P.	Wt. %.
Ag99 (1)	54.99	1100° ± 50	2½ hrs.	5.19	22.11	27.57	0.12	16.25		2.32
Ag99 (2)	58.89	1260°	5¾ hrs.	4.74	24.00	30.01	0.14	16.74		2.39
(O ₂ sat.)										
Ag99	56.90	1226°	3 hrs.	5.76	24.80	26.19	0.15	18.16		2.59
English	43.79	1412°	2¼ hrs.	2.76	18.36	22.56	0.11	11.94		1.71
German	201.00	1412°	3¼ hrs.	9.76	32.92	154.5	3.79	26.25		3.75

The data in this table show that the larger part of the oxygen held by the charcoal had been fixed before the samples had been "soaked" in pure oxygen. A comparison of the amounts of oxygen which is fixed by the different charcoals with the amounts adsorbed is given in Table III, together with the ratio of fixed to adsorbed oxygen. This shows that as much as 6 times the amount of oxygen adsorbed by a charcoal may be held as "fixed" oxygen.

TABLE III.

	Cc. N T. P. oxygen per g. of charcoal.		Ratio of fixed to adsorbed O ₂ .
	Fixed.	Adsorbed.	
Ag99.....	18.16	7.2	2.5
English.....	11.94	8.6	1.4
German.....	26.25	4.2	6.3

In Table IV are given the actual observations on a run, in order to give an idea of how an experiment proceeded, after the sample had been thoroughly outgassed at 200°.

TABLE IV.
Sample Used—A909 = 2.948 g.

Time.	Cc. gas.	Temp.	Time.	Cc. gas.	Temp.
2 : 05	0.00	25°
2 : 15	97.4	959	3 : 45	2.5	1190°
2 : 25	19.0	1045	3 : 55	1.7	1226
2 : 35	13.0	1091	4 : 05	1.2	1208
2 : 45	17.0	1160	4 : 15	1.10 ^a	1196
2 : 55	10.5	1178	4 : 25	1.06	1211
3 : 05	10.0	1172	4 : 35	0.90	1211
3 : 15	6.0	1181	4 : 45	0.72	1205
3 : 25	4.0	1196	4 : 55	0.61	1211
3 : 35	2.7	1166	5 : 05	0.46	1208

^a These small volumes were measured in the fall tube of the Töpler pump (*J. Ind. Eng. Chem.*, 12, 40 (1920)).

At the end of each determination, the walls of the quartz tube held on their inner surface a thin film of a solid varying in color from white to brown, which had vaporized from the charcoal at the high temperatures. A similar observation has been recorded by A. Schuller,¹ who concluded that this was organic matter. On attempting to remove this film, however, the odor of acetylene was noticed. This suggested that a carbide had been formed during the determination and that accordingly some of the oxides of carbon obtained might well have been from reduction of mineral matter contained in the ash. In order to determine what might be the magnitude of this effect on the data obtained, the percentage of ash was determined for each charcoal and the ash analyzed. In the A909 and English charcoals this was mostly alkali carbonates with slight traces of alkaline earths, iron, and alumina. In the German charcoal the ash was principally iron with some alkali carbonates. Table V presents this

TABLE V.

	% ash.	Calc. cc. O ₂ per g. of charcoal.	Cc. O ₂ remaining "fixed" by charcoal.
A909.....	1.11	3.00	15.16
English.....	2.04	5.41	6.53
German.....	1.91	4.35	21.90

data and the maximum amount of oxygen which could under any circumstances be attributed to the ash. It is thought, however, that the amount of reduction at these comparatively low temperatures was in all cases much less than these figures would indicate. In any case, as shown in this table, the ash can account for only a small part of the oxygen obtained in the experiments as oxides of carbon.

Discussion.

Since it has been definitely shown that oxygen can be "fixed" by charcoal, other than by adsorption, it becomes an interesting problem to consider the origin and state of this oxygen. The original material from which

¹ Schuller, *Wied. Ann.*, 18, 317 (1883).

all these charcoals were prepared was organic matter and as such contained in the molecular complexes both oxygen and hydrogen. It seemed possible that *both* the oxygen and hydrogen obtained by us were from some of the original material which had not been decomposed in the preparation of the charcoals, but against this view we find the following facts. The temperature of charring this original material was in all cases very close to the temperature, above which no oxides of carbon were obtained and only above which hydrogen and methane were obtained. This would lead us to the conclusion that the hydrogen alone was from the original undecomposed organic material. This conclusion is supported by the fact, which was pointed out in the introduction, that the oxygen obtained as oxides of carbon on heating in a vacuum was reversible while the hydrogen was irreversible. An actual experiment showed that 90% of the oxygen obtained as oxides of carbon above 184° was fixed by the charcoal a second time in 99 hours. On the other hand, in every case hydrogen admitted to a charcoal after outgassing at 1050° and cooling to room temperature could be readily and quantitatively recovered at room temperature.

In view of these facts, we have concluded that this fixed oxygen is held by the charcoal as a surface compound or compounds. These compounds would be, therefore, solid oxides of carbon high in carbon and low in oxygen content, but not necessarily in which the ratio of carbon to oxygen was constant. These oxides must be stable at ordinary temperatures, or at least have a very low rate of decomposition, the decomposition not taking place appreciably until a temperature of about 200° is reached. The data shows that these oxides then break down slowly, giving carbon dioxide and carbon monoxide and presumably leaving a residue of carbon. Although the carbon dioxide predominates at the lower temperatures in the decomposition and carbon monoxide at the higher, no conclusions as to the mechanism of the original decomposition can be made, since carbon dioxide liberated in immediate contact with carbon at the higher temperatures would react immediately with the carbon and be reduced to the monoxide, *i. e.*, there would be a tendency to attain equilibrium between carbon, carbon monoxide and carbon dioxide at any given temperature.

This conception of a solid oxide of carbon, stable at ordinary temperatures, is not new. Brodie¹ isolated 2 oxides of carbon which were amorphous, brown and transparent solids to which he assigned the formulas C_5O_4 and C_4O_3 , and indicated that he considered that they belonged to a series of oxides corresponding to the hydrocarbons of the acetylene series. Berthelot² showed that these oxides decomposed on heating to 300° in an

¹ Brodie, *Ann.*, 169, 270 (1873).

² Berthelot, *Bull. soc. chim.*, 26, 102 (1876).

atmosphere of nitrogen to an oxide still higher in carbon content by loss of equal volumes of carbon dioxide and carbon monoxide and to which he assigned the formula $C_{18}O_6$. Mellitic anhydride, $C_{12}O_9$, has recently been prepared and its properties described in 2 independent investigations.¹ The most recent work on graphitic acid² and work done in this laboratory (which has not yet been published) indicates that this is a colloidal oxide of carbon with an empirical formula approaching C_8O .

Furthermore, H. E. Armstrong,³ in his studies on the combustion of carbon, concluded that the simple oxides, carbon dioxide and carbon monoxide, were obtained only by the breakdown of the more or less completely oxidized carbon complex. The later extensive researches of Rhead and Wheeler⁴ on the same subject lead to the conclusion that oxygen combines with a mass of carbon directly to form a "physico-chemical" complex C_xO_y of variable composition, which is decomposed by heat into carbon monoxide and dioxide. These investigators performed some interesting experiments to determine the amount of this solid carbon-oxygen complex present at temperatures from 100° to 900° during the combustion of carbon. Their results indicate that the higher the temperature, the less the amount of the complex present. If we extrapolate their results, it would appear that at room temperature practically no carbon monoxide or dioxide would be formed but only the complex, while above about 1200° very little of the complex would be formed. This agrees entirely with our observations, which, interpreted by means of assuming the formation of this C_xO_y complex, shows that the first stage in the combustion of carbon takes place at ordinary temperatures. Langmuir⁵ has shown that a similar complex of carbon and oxygen, presumably an extremely stable solid oxide of carbon, was formed by a highly graphitized filament of very pure carbon. This decomposed only slowly at 1425° but readily at 1925° and seems to have been even more stable than the complex formed by oxygen with amorphous carbon. These facts all indicate that oxygen does combine with carbon to form a complex, C_xO_y , high in carbon and low in oxygen content, which decomposes on heating to give the ordinary oxides of carbon.

We are led further to the conclusion that this complex must be formed on the surface of the charcoal. This would therefore be likely to alter the adsorptive capacity of a charcoal, which would thus depend in part on the amount of this complex on the surface. No conclusive data on this point have been collected, however, since, although it was observed

¹ Meyer and Steiner, *Ber.*, **46**, 813 (1913); and Jarrad, *J. Chem. Soc.*, **29**, 106 (1913).

² Kohlschütter and Haenni, *Z. anorg. Chem.*, **105**, 121 (1919).

³ Armstrong, *J. Soc. Chem. Ind.*, **24**, 473 (1905).

⁴ Rhead and Wheeler, *J. Chem. Soc.*, **101**, 831 (1912); and **103**, 461 (1912).

⁵ Langmuir, *J. Am. Chem. Soc.*, **27**, 1154 (1915).

that the adsorptive power of the German charcoal with the most fixed oxygen was the lowest and the English charcoal with the least fixed oxygen the highest, the presence of undecomposed hydrocarbons was also greatest in the German and least in the English charcoal. So, since in the preliminary treatment of the charcoals (Part I), most of the fixed oxygen was removed while the hydrocarbon content was not much altered, the differences observed are more likely due to this latter cause.

Conclusions.

1. The anomalous behavior of the adsorption of oxygen by charcoal extending over long periods of time, overlooked by recent investigators, has been confirmed. This is shown to be due to the presence of 2 phenomena, adsorption and surface combination.

2. A method has been developed for heating charcoal in a vacuum out of contact of oxygen-containing materials, as quartz, to high temperatures by use of the Northrup induction furnace. The gases evolved were collected and analyzed.

3. The formation of a carbon-oxygen complex, essentially a stable solid oxide of carbon, has been shown to occur on the surface of charcoal at ordinary temperatures. This complex decomposes on heating to carbon dioxide and carbon monoxide and can thus be considered to be an intermediate step in the combustion of charcoal, which supports the view suggested by Armstrong and supported with experimental evidence by Rhead and Wheeler and by Langmuir.

4. The amounts of oxygen thus combined to the charcoal has been found to vary with 2 samples of charcoal from 1.71% to 3.75% of the *weight* of the charcoal.

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